PREPARATION, CHARACTERIZATION AND APPLICATIONS OF SILVER SULPHIDE QUANTUM DOTS

Synopsis

Submitted in partial fulfillment of the requirements for the award of the degree of

Doctor of Philosophy

in

Chemistry

Submitted by

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Enrollment No.: H13219

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2019-2020

1. Introduction

The QDs (Quantum Dots) were discovered by the Russian physicist Alexei Ekimov and Luis Bruis while working with colloidal nanocrystals [1]. Colloidal semiconductor nanocrystals are extremely important and interesting due to their potential applications of biomedical marking [2]. Semiconductor QDs have been extensively studied due to their interesting characteristics from both basic research and practical viewpoints [3]. Quantum dots are nanocrystals made of pure minerals and / or three-dimensional semiconductor alloys, the size of which ranges from 1 to 10 nanometers [4]. Semiconductor QDs have unique optical properties due to adjustable emission spectra [5]. QD is structurally and electrically isolated from the outside [6]. QDs and many colloidal semiconductor nanostructures becomes a promising candidate for applications in optical stimulation technology, which have caused extensive and accurate absorption in the visible range, low wavelength, and functional chemistry by the organic bonds [7]. Structurally QDs have a metallurgical crystalline core and a lid or shell that covers and protects the core and makes QD bio-available. These cores can be made of different material. In all synthesis approaches, the surface of QDs is passivized (during or after synthesis) by external agents forming a layer of functional groups or molecules which bind to the carbon nucleus [8].

Silver Sulphide Quantum Dot (Ag_2S QDs)

Silver sulphide QDs have recently appeared as new generation QDs [9]. Silver sulphide QDs has become unique nanomaterial's that demonstrate unprecedented advantages and superior biomedicine properties due to their unique structural and physicochemical properties [10]. Silver sulphide QDs is a promising candidate for the detection of metal ions because of its low toxicity and attractive fluorescence ability, covering the area between the red and near infrared (NIR) [11]. Quantum dots (QDs) have become a popular means of visualization, competing with other fluorescent nanomaterials and other coatings (dyes) [12]. Silver sulphide (QD) quantum dots have a keen interest in recent years due to their infrared (NIR) attraction with infrared light (PL) in another window (NIR-II, 1000-1400 nm), which gives a deeper insight into imaging in vivo penetration and greater ratio with noise signal against optical probes in NIR-I window (650- 950 nm) [13]. The family of the future QDs for biomedical applications (especially in NIR) is the chalcogenides of silver QDs (Ag_2X, with X = S, Se, Te) having less toxicity compared to normal QDs. In addition, high solubility is presented by silver chalcogenides QDs them to obtain minimum Ag ion in the desired applications.

QDs of silver chalcogenides have a narrow band gap, which is approximately 0.9–1.1 eV for Silver sulphide [4]. Silver sulphide are the non-toxic QDs, possess the potential for imaging of microbial organisms in the highly and pH detection [14]. Silver sulphide QDs has emerged as a unique nanomaterial that demonstrates unforeseen benefits and better performances in biomedical due to its unique structural and physico-chemical features [11]. Structurally, the ordinary QDs are a metalloid crystalline core covered by an outer organic layer [15]. Preparation of non-toxic NIR- emitting QDs that emit directly into aqueous solution will greatly simplify the preparation [16]. Recently, silver sulphide (Silver sulphide) QDs have been shown to, for the first time, be an attractive alternative to traditional NIR-II-emitting in vivo due to photoluminescence in the NIR-II region (1.0-1.4 μm), having greater efficiency and good biocompatibility. Major efforts have been focused on acquiring various synthetic methods associated with Silver sulphide QDs [17]. Silver sulphide QDs are a promising candidate for the detection of metal ion due to its very low toxicity i.e. negligible toxicity and attractive fluorescence properties covering the region between red and near infrared (NIR). Silver sulphide photoluminescence emission quantum dots could be tuned from 510 to 1221 nm [18]. Imaging includes the realization of all types of diagnostic and therapeutic tests where equipment is used to obtain images of an organism [19]. Silver sulphide QDs is applied to detect the cancer cell MCF-7. Breast cancer cells are called as MCF-7 cells and these cells make an over exploitation of their membrane [20].

2. Literature Review

Jiang *et al*., [2012] synthesized water soluble silver sulphide QDs by one step method and reported the water soluble silver sulphide QDs which were terminated with carboxylic acid. Water soluble silver sulphide QDs were successfully synthesized using simple precursor (3-mercaptopropionic acid and silver nitrate). The photoluminescence emissions were tuned in the range from 510nm to 1221nm by modulating the growth time. The prepared silver sulphide QDs were successfully used for small animal in vivo imaging [2].

Jiang *et al*., [2012] synthesized small sized QDs by injecting hexamethyldisilathiane into the mixture of silver acetate, myristic acid, 1-octylamine, and 1-octadecene at a given temperature under argon flow and they reported the large-sized silver sulphide QDs by seed- mediated growth, by drop wise addition of Ag (OA) solution ($AgNO_3$ and OA dissolved in toluene) and sulphur solution (sulphur powder dissolved in toluene) in to a toluene solution containing small-sized Silver sulphide QDs [21].

Hocaoglu *et al.*, [2012] prepared colloidal stable and highly luminescent near – IR emitting

Silver sulphide QDs by a simple aqueous method using 2-mercaptoprionic acid as a coating. They reported that emission of Silver sulphide-2MPA near – IR QDs can be tuned between 780 nm and 950 nm. The near – IR QDs have photoluminescence quantum yields around 7-39% and exhibit excellent cyto-compatibility even at 600 μg mL^{-} in NIH /3T3 cells. With such improved properties, Silver sulphide-2MPA NIRQDs has a great potential in practical bio- applications [22].

Yang *et al.,* [2013] reported a facile and one-pot biomimetic synthesis approach to prepare water-dispersible NIR-II- emitting ultra-small Silver sulphide quantum dots. Photoluminescence spectra showed that the emission peaks could be 1294 to 1050 nm as the size of the Silver sulphide quantum dots varied from 6.8 to 1.6 nm. The x-ray diffraction pattern and x- ray photoelectron spectra confirmed that the products were monoclinic α-Silver sulphide. Fourier transform infrared spectrograph analysis indicated that the products were protein –conjugatedSilver sulphide quantum dots [17].

Zhao *et al.,* [2014] reported the facile phase transfer based synthesis to achieve water dispersed NIR-II emitting Silver sulphide QDs. After undergoing phase transfer of Ag^{+} ions from water to toluene, and the synthesis of Silver sulphide in toluene followed by ligand exchange, Silver sulphide QDs were favorably prepared. A series of characterizations confirmed that the prepared products were monoclinic α- Silver sulphide, showing an average size of 3.7 nm. The Silver sulphide QDs exhibited the maximum emission located at 1045 nm, high PL stability and low cytotoxicity, facilitating their biomedical applications, indicating the feasibility of Silver sulphide QDs for effective bio imaging in NIR-II biological window [23].

Arthur *et al.,* [2014] synthesized the silver sulphide quantum dots by using SILAR (successive ionic layer adsorption and reaction) technique. Different number of SILAR circles ranging from four to ten circles of Silver sulphide QDs was synthesized. Tin II chloride solutionwas used as the reducing agent which reduces silver hydroxide to silver. A colorlesssubstrate immersed in the container of Tin II chloride solution before its immersion in the container of silver nitrate solution was observed to be brown which increases with thenumber of SILAR cycles as a result of the formation of silver QDs on it. The number of cycles directly determines the size of the QDs produced. Exposure of these substrates with silver QDs to hydrogen sulphide for 10 minutes in a fume chamber using the Kipp's apparatus converted the silver quantum dots to silver sulphide quantum dots thereby making the substrates to become dark brown. The synthesized QDs were characterized using UV-

SPEC2048 spectroscopy machine. The dots were found to have high absorbance in the UV-region and depreciate as the wavelength increased. They have high transmittance in the visible near infra-red region [24].

Maji *et al.,* [2014] synthesized highly mono-dispersed silver sulphide QDs with an average size of 11nm from a single –source precursor, and they aimed to employ them as electrode materials for the detection of phenol. The prepared silver sulphide QDs are immobilized on a glassy carbon electrode, and the electrochemical sensing of phenol. Prepared silver sulphide QDs were immobilized on a glassy carbon electrode and the electrochemical sensing of phenol using the developed silver sulphide QDs/ GC electrode were observed to be within a wide range. A novel non enzymatic aerometric sensor has been constructed by coating silver sulphide QDs on GC electrode [25].

Stanislav *et al.,* [2016] prepared stable colloidal solutions of Silver sulphide quantum dots in the dark from reaction mixture with sodium sulphide concentration $C_{Na2S} = (C_{AgNO3}/2) + \delta_{1,}$ where δ_1=0.01. The stability of these colloidal solutions was confirmed by their zero turbidity immediately after synthesis. Measurements showed that the turbidities of these solutions after2, 5, 8, 11, 16, 24, 32, 40, 60 and 100d were still equal to zero [26].

Wu *et al.,* [2017] had developed a facile two-step route to synthesize the water-soluble Silver sulphide quantum dots, constituting of a green hydrothermal process and followed surface ligands exchange. Surface passivation was proposed to be the mechanism for the enhanced fluorescence. They successfully reported the simple and facile strategy for synthesis of water-soluble Silver sulphide quantum dots, which exhibit excellent fluorescent properties in the second near-infrared window. More importantly, it is demonstrated that the prepared Silver sulphide quantum dots have highly selective detection of Zn^{2+} and Cd^{2+} in a ‒turn on‖ model. With the advantages of easy preparation, low cost, high sensitivity, less intensity loss and weak background noise, the NIR-II fluorescent Silver sulphide QDs show excellent potential in the field of ion detection [27].

Kozhevnikova *et al.,* [2017] reported one-pot inorganic route to highly stable water-dispersible Silver sulphide quantum dots. They reported the low temperature one-pot route for obtaining highly stable aqueous colloid solutions of Silver sulphide QDs, using NH_3 molecule as monodentate ligand. This low-temperature strategy was based on one-pot synthesis using water solutions as precursors and without using any inert atmosphere. The surface of Silver sulphide QDs was hydrophobic, and their stability in aqueous media was hindered by aggregation and sedimentation phenomenon. The Silver sulphide QDs obtained

in this study were prepared through precipitation reaction between Ag $(NH_3)_2^+$ and HS^-, followed by immediate interaction of negatively charged Silver sulphide QDs with $NH_3.H_2O$ as covalent ligand and pH adjuster. NIR-II Silver sulphide QDs were directly synthesized in aqueous phase through a facile and rapid non injection organic method [18].

Zhao *et al.*, [2019] had synthesized the core/shell Silver sulphide QDs by seed-mediated growth methods showed a good linear relationship between fluorescence intensity and pH value in the range 2.1-7.2. $AgNO_3$ is reacted with $S\text{-}N_2H_4$ at 57˚C in the presence of cys PC_{10} Acyscys which leads to formation of Silver sulphide seed then it was treated by HCl at room temperature and pH <4. In addition the core/shell Silver sulphide QDs exhibited excellent reversibility and good biocompatibility, which can serve as multifunctional probes for the imaging and detecting of Gram-negative bacteria without the influence of auto fluorescence in the extremely acidic environment [15].

Lu *et al.*, [2019] reported a facile one-pot approach for the synthesis of NIR-II emissive Silver sulphide quantum dots. The effect of ligand was carefully investigated to improve the quality of QDs. It is found that the QDs tend to form clusters when 1-dodecanethiol was used as the only ligand. The addition of oleic acid can greatly improve the dispersity of the nano crystals but lead to a significantly decrease of the emission intensity. Best Silver sulphide QDs were obtained after oleic acid and small amount of oleylamine were introduced into a reaction system, which exhibited both good dispersity and strong emission in the second near-infrared window. Hydrophilic Silver sulphide QDs were obtained by ligand exchange with mPEG-SH. Whole body blood vessel imaging and tumor imaging was achieved with these PEGylated Silver sulphide QDs*in vivo* [28].

Zhao *et al.*, [2019] synthesized genetically engineered polypeptide capped Silver sulphide quantum dots. Three kinds of cysteine were integrated to the C-terminal and N-terminal of $RGDPC_{10}A$ to enhance the stability and brightness of the synthesized Silver sulphide quantum dots. And they reported that $RGDPC_{10}$ capped Silver sulphide quantum dots exhibited excellent stability, outstanding resistance to photo bleaching, and superior quantum yield up to 3.78% in the NIR-II biological window. The in vitro and in vivo results showed that the $RGDPC_{10}A$ capped Silver sulphide quantum dots possessed typical NIR-II fluorescence, photo acoustic imaging, and photo thermal therapy effect of tumor [29].

3. Research Gap Identification

In fact, many researchers have studied the synthesis of Cadmium, Lead, Zinc quantum dots by different methods. Silver Sulphide QDs have been synthesized by many researchers mostly by chemical methods and that need a post treatment to become hydrophilic. There is very less literature on the preparation of silver sulphide quantum dots by the aqueous methods. Therefore in this work we have planned to synthesize the silver sulphide quantum dots by using precursor of silver nitrate.

4. Objectives

The main aim is to study the quantum dots of silver sulphide, encapsulation of silver sulphidequantum dots by polymer and the applications of silver sulphide quantum dots.

- **a.** To synthesize the silver sulphide quantum dots.
- **b.** To encapsulate silver sulphide quantum dots by polymer.
- **c.** To characterize silver sulphide quantum dots.
- **d.** To study the applications of encapsulated as well as non-encapsulated quantum dots.

5. Proposed Methodology

Chemicals Required

Chemicals required for the synthesis of Silver Sulphide Quantum Dots are Silver nitrate ($AgNO_3$), Ammonia (NH_3), 3-Mercaptopriponic acid ($C_3H_6O_2S$), Distilled Water (H_2O), Thiourea (CH_4N_2S), and Polymer.

Apparatus Required

Apparatus used for the synthesis of silver sulphide quantum dots are magnetic stirrer, beaker,Thermometer, pH meter, measuring cylinder.

Experimental Procedure Synthesis of Silver Sulphide QDs

To synthesize silver sulphide QDs, Silver nitrate is dissolved in distilled water in a thoroughly manner. After that ethylene glycol is added and then we have to fix the pH by using ammonia solution. This process will followed by addition of thiourea at optimized temperature. And then we will stir as well as heat the solution for 2-3 hours. Synthesis willbe followed by washing and centrifugation for removing byproducts from mixture.

Encapsulation of Silver Sulphide QDs

To stabilize silver sulphide QDS we will encapsulate the surface of prepared Silver Sulphide QDs with the help of polymer like PEG (Polyethyleneglycol).

Antibacterial Activity

Antibacterial activities of Silver sulphide QDs will be tested with the help of well diffusion method by using *Staphylococcus aureus* (MTCC 737), *Bacillus subtilis (*MTCC 441), *Pseudomonas aeruginosa* (MTCC 1688). Test organisms will be collected from Institute of Microbial Technology, Microbial Type Culture Collection Centre, (IMTECH), Chandigarh. Mueller-Hinton agar will be poured in the sterilized petri plates and allowed to solidify. The plates will be left over night at room temperature to check for any contamination to appear. Bacterial strains will be spread on Mueller-Hinton agar plates and produced the hole with the opposite side of tip. The prepared Silver sulphide QDs suspension will be added into the wells. These samples initially incubated at 37°C for 24 h. After incubation period, the zone of inhibition of each well will be measured and the value will be recorded, average values willbe calculated for the eventual antibacterial activity.

Characterization of Silver Sulphide Quantum DotsUltra-Violet (UV) Spectroscopy

Spectroscopy in the ultraviolet, visible and near infrared region of the electromagnetic spectrum is often called electronic spectroscopy because electrons are transferred from low-energy to high-energy atomic or molecular orbitals when the material is irradiated with light. Such electron transfer processes may take place in transition metal ions, and inorganic and organic molecules. They are responsible for the color of the matter. The interaction of light ofthe UV-Vis-NIR region with catalytic solids is considered to be a complex process due to absorption and scattering phenomena [30].

X-Ray Diffraction (XRD)

XRD techniques have a number of advantages in forensic work and in the examination of documents; they are rapid, non-destructive and applicable to both very large and very small samples. In many cases the minerals used as filters in paper-making may also are identified by XRD. A certain amount of the information obtained by XRD can also be obtained by elemental analysis. However XRD supplies information not obtainable by other methods.

Transmission Electron Microscopy (TEM)

Optical microscopy and scanning electron microscopy are common techniques in mineralogical and structural investigations of geological and archaeological samples. The more complex and advanced transmission electron microscopy so far has been rarely used in geological and archaeological research. TEM is used together with other analytical methods in a comparative study of ancient pottery to identify copper- and iron-based

pigments, to characterize the microstructures of opaque glass mosaics from a mediaeval church in Italy. A promising area of application for TEM, important to geology and archaeology, is to products of combustion [31].

Photoluminescence (PL) Spectroscopy

Photoluminescence (abbreviated as PL) is the emission of light from any form of matter after absorption of photons (electromagnetic radiation). It is one of many forms of luminescence (light emission) and is initiated by photo excitation (i.e. photons that excite electrons at a higher energy level in an atom), hence the prefix photo. After excitation, various relaxation processes occur in which other photons are re-irradiated. The time periods between absorption and emission can vary: from a short femtosecond rate for emission involving free transporter plasma in inorganic semiconductors to milliseconds for phosphorescence processes in molecular systems; and in special circumstances, the broadcast delay may even extend to minutes or hours.

Fourier-Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique used to obtain an absorption or emission infrared spectrum of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range.

Energy-Dispersive X-Ray Spectroscopy

This spectroscopy is used to identify elements of unknown composition. The emission spectra of molecules can be used in the chemical analysis of substances. This technique isalso called as EDS.

6 Thesis Outline

Chapter 1 (Introduction): This chapter will include the detail about quantum dots and the silver sulphide quantum dots**.**

Chapter 2 (Literature Review): This chapter will deal with the intense literature survey of silver sulphide quantum dots.

Chapter 3 (Experimental and Characterization Techniques): This chapter will describe the material and apparatus used for synthesis of silver sulphide quantum dots and the characterization techniques to be used.

Chapter 4 (Result and Discussion): This chapter will describe detail discussion on results of present work of synthesized silver sulphide quantum dots and its applications .

Chapter 5 (Conclusion): This chapter will comprise summary of entire study according to objectives along with conclusions.

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